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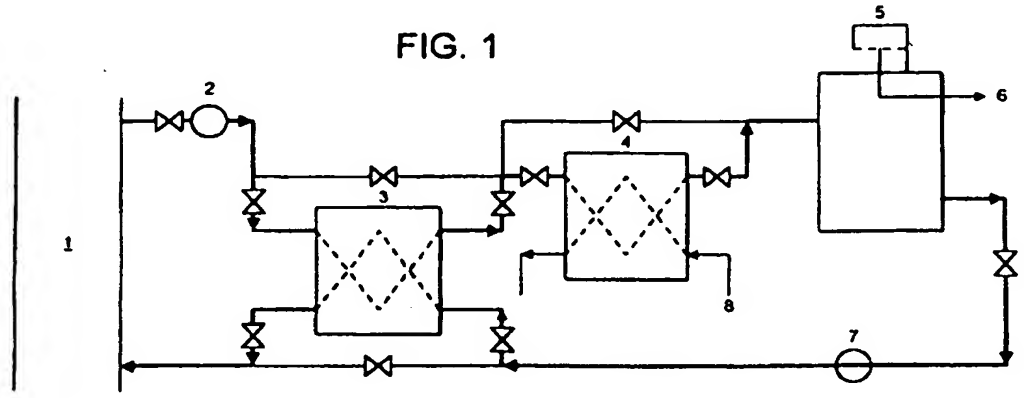
(54) **Freeze distillation process and product**

(57) The process, which is for preparing "freeze distilled" alcohol for use in beverages such as vodka, comprises the partial or complete removal of fusel oil (i.e. >C2 alcohols) from an aqueous, alcoholic fraction taken from a distillation column at 80-95°C by (a) cooling the fraction to below c. 0°C to reduce the solubility of the fusel oil therein, and preferably rendering it substantially insoluble; (b) separating the aqueous fraction from the fusel oil; and (c) returning the aqueous fraction to the distillation. Apparatus for carrying out the process comprises a distillation column 1, a pump 2, heat exchangers 3 and 4 (in the latter of which the fraction is cooled to -10°C by ammonia 8), a separation tank 5 and a pump 7.

FIG. 1



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At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

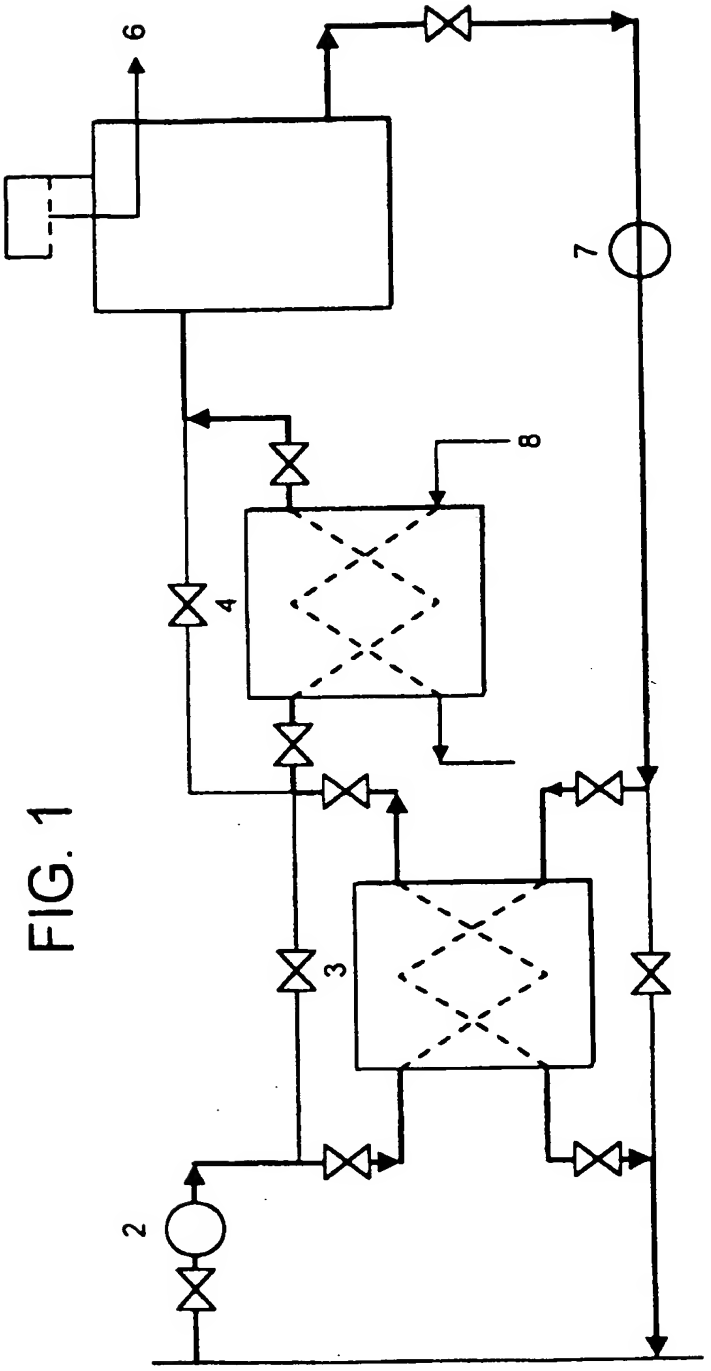

FIG. 1

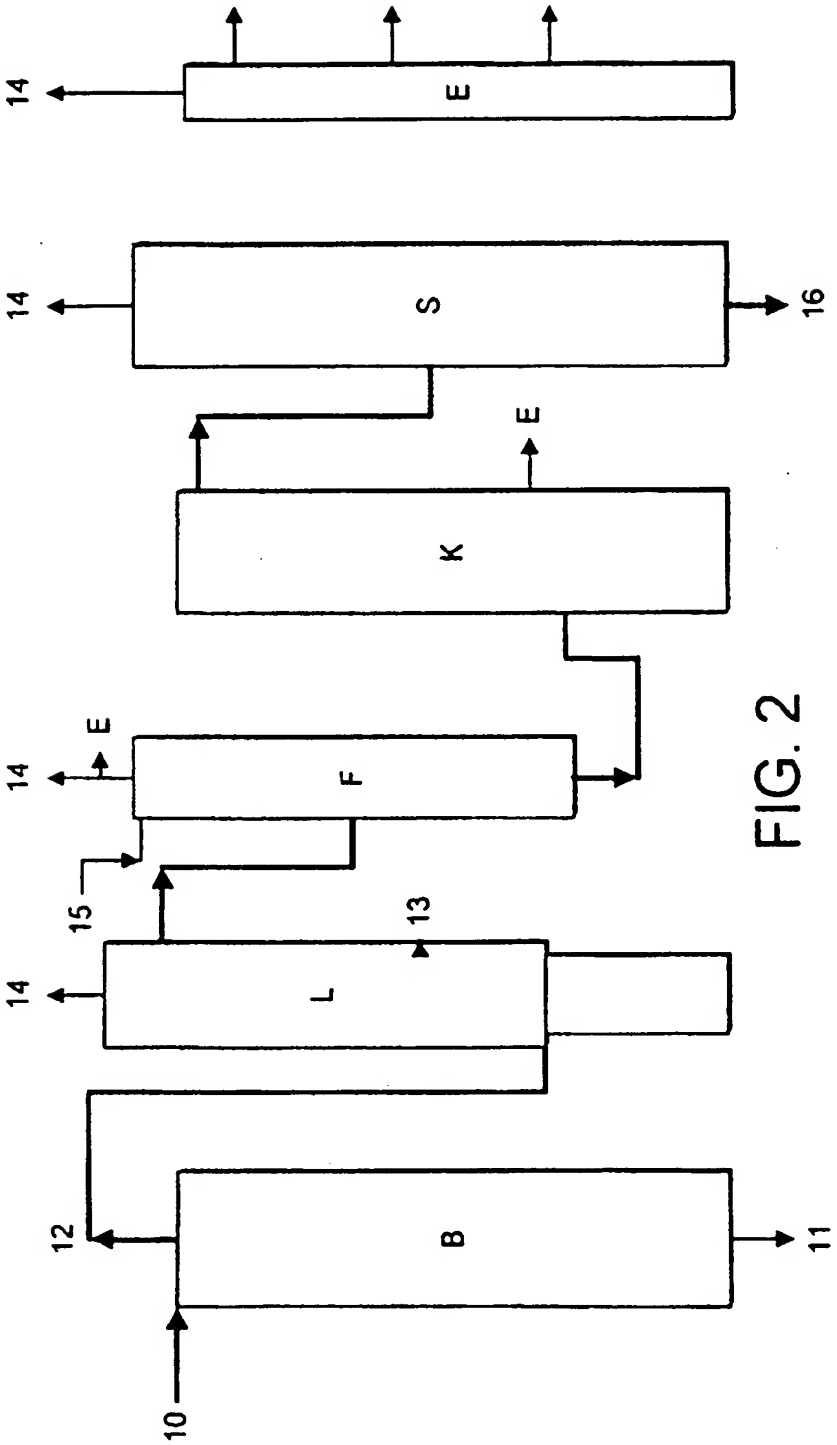

FIG. 2

Distillation Method

The present invention relates to a distillation method.

When producing ethanol by fermentation, alcohols with more than two carbon atoms, such as 2-Methyl-1-Propanol, 3-Methyl-1-Butanol and 2-Methyl-1-Butanol are formed during the fermentation process. Within the fermentation industry these alcohols are generally known as fusel oil.

Fusel oil imparts an characteristic odour and taste to ethanol and is therefore traditionally removed therefrom during the distillation process. The removal of fusel oil from distilled ethanol has hitherto taken place by removing a fusel oil-containing fraction from the distillation column where the liquid phase has an alcoholic strength of 40-50% v/v. At this strength the fusel oil, which is soluble in ethanol but less soluble in aqueous mixtures, is kept dissolved in the eyhanol/water mixture. In order to remove it, it has been necessary to add $1^1/_2$-2 volumes of water to the fraction in order to separate the fusel oil from the alcohol by rendering it insoluble in the ethanol/water mixture. Having a lower density, the fusel oil rises to the surface of the separation vat from where it can be drawn off, while the diluted ethanol/water mixture can be recycled to the distillation column.

There are several disadvantages associated with this system. For example, the continuous addition of water to the distillation process requires the input of additional energy in order to maintain a sufficient distillation temperature in the distillation column. An increase in the volume of waste water present in the bottom of the column will also occur, which can lead to capacity restrictions. Moreover, impurities in the added water may be deposited on the walls of the distillation column, which accordingly requires more frequent cleaning.

International Patent Application WO94/21779 (Labatt Brewing Company Limited) describes a process for brewing fermented malt beverages, typically beer, in which a freezing step is used in order to cause ice crystal formation in the beer. The object of

this process is to prevent "chill haze" and other problems normally associated with beer. Due to the formation of ice crystals during the chilling process, beers produced by such methods are often referred to as "ice" beers. The process effectively allows the removal of water from the brew but is not suitable for removal of fusel oil.

The present invention overcomes the problems of the prior art by providing a method for preparing a distilled alcohol or a distilled alcoholic beverage which comprises the removal of fusel oil contaminants at a reduced temperature.

According to a first aspect of the present invention, there is provided a process for removing fusel oil from an aqueous alcoholic medium, comprising the steps of:

(a) cooling the medium to effect separation of fusel oil from the medium; and

(b) removing at least part of the fusel oil from the medium.

A fusel oil, as referred to herein, is an alcohol or mixture of alcohols having more than two, typically four or more, carbon atoms, whose presence in alcoholic solutions may be undesirable on account of its characteristic effect on taste and/or aroma. By reducing the temperature of alcoholic aqueous media containing fusel oil, the solubility of the fusel oil in the solution may be reduced, to the point where it no longer remains in solution. The fusel oil being lighter than aqueous alcohol, the medium separates into two phases, and the fusel oil phase may be removed. A better separation of fusel oil from the alcoholic aqueous phase is thus obtained than is possible through conventional dilution processes.

Agricultural alcohol is produced by distillation of a variety of raw materials from agricultural sources, for example potato and grain. This spirit is the basis of a variety of alcoholic beverages, such as bitters, aquavit, gin and vodka. The production of, for example, aquavit, may require a second distillation step, and have flavouring substances added thereto, while others, such as vodka, may be subjected to only a single distillation, and possibly also a filtration step.

As used herein, "Agricultural alcohol", "ethanol" and "spirit drink", as well as "vodka" and the specific names of other alcoholic beverages, are as defined in EC Directive 1576/89 of 29th May 1989, incorporated herein by reference. "Ethanol" is synonymous with "ethyl alcohol", and "agricultural alcohol" is synonymous with "agricultural ethyl alcohol".

The removal of fusel oil according to the present invention is carried out during the distillation. An alcoholic aqueous fraction containing fusel oil is removed from the distillation apparatus, which is typically a distillation column, and subjected to fusel oil removal before being returned to the distillation apparatus. Fraction removal may be iteratively repeated but is preferably operated continuously throughout the distillation process.

The alcoholic aqueous fraction preferably has an alcohol content of 10% v/v or more. Advantageously, it is between 10 and 40% v/v. Preferably, the alcohol content is between 20 and 30% v/v. The concentration of alcohol is thus lower than in the dilution methods used in the prior art.

Advantageously, the alcoholic aqueous fraction is removed at a temperature of between 80 and 98°C, preferably between 85 and 95°C, and most preferably at or around 90°C, at atmospheric pressure.

The alcoholic concentration and the temperature of the fraction removed from the distillation are linked. Thus, an aqueous alcoholic fraction removed from a grain distillation with a strength of 10% v/v will have a temperature of about 92°C, while a 40% fraction will have a temperature of about 82°C, at atmospheric pressure. Different temperatures may be applicable at other pressures.

The alcoholic aqueous fraction may be cooled in one or more steps. For example, an efficient way initially to reduce the temperature is to pass the fraction issuing from the distillation apparatus to a first heat exchanger, wherein heat exchange takes place against processed aqueous alcoholic fraction material from which fusel oil has already

been removed and which is being returned to the distillation apparatus. Alternatively, or, preferably, in addition, the fraction may be further cooled by refrigeration or further heat exchange steps. The fraction may be cooled by any suitable means, such as refrigeration using coolants such as liquid nitrogen, but preferably it is cooled by ammonia evaporation.

The fraction is preferably cooled to below about 0°C, more preferably -5°C to -15°C, and advantageously around -10°C.

Fusel oil contained in the alcoholic aqueous fraction is preferably rendered substantially insoluble at the reduced temperature, and may be removed, for example by tapping off the fusel oil fraction in a separator vessel. The fusel oil being less dense than the alcoholic aqueous fraction, it rises to the top and may be removed from the surface of the alcoholic aqueous fraction.

By "substantially insoluble", it is intended that the fusel oil becomes insoluble in the alcoholic aqueous mixture to a point where it begins to come out of solution and form an independent liquid phase. This can be removed as described, for example in a separation vat.

Clearly, by chilling the alcoholic aqueous phase further, the fusel oil may be more efficiently removed therefrom, since its solubility therein will be further reduced. Since the application of a low temperature step is necessary in the process according to the invention, it is referred to as freeze distillation.

In a preferred embodiment, therefore, the invention provides a freeze distillation process for preparing a freeze distilled alcohol, the process comprising partial or complete removal of fusel oil by the steps of:

(a) removing an alcoholic aqueous fraction comprising alcohol and fusel oil from the distillation;

(b) cooling the fraction to reduce the solubility of the fusel oil therein, rendering it substantially insoluble; and

(c) separating the aqueous fraction from the fusel oil, and returning the thus separated aqueous fraction to the distillation.

As used herein, "freeze distillation" refers to a distillation process in which fusel oil is removed according to the invention as described above.

The distillation process may include further steps, depending on the final product which it is intended to produce. Thus, further distillation steps, optionally with flavourings, filtrations and the like may be included. Optionally, the distillation process may yield a spirit drink directly. In a preferred aspect, the invention provides a distillation process for the production of agricultural alcohol which involves the use of six distillation columns, namely an analyser, a rectifier, a hydroselection column, a concentration column, a finishing column and a feints and heads column. The alcohol is obtained at the bottom of the finishing column, and preferably has a strength of at least 96% v/v.

Further processing of the agricultural alcohol into a spirit drink, for example in the production of vodka, may involve dilution with water. For producing vodka, the use of softened mineral water is preferred, although demineralised water may also be used.

According to a second aspect of the invention, there is provided a freeze distilled alcohol. As used herein, a "freeze distilled" substance is an substance at least part of which is an alcohol which has been produced by a method as described in the first aspect of the invention. In a most preferred embodiment, the alcohol is ethanol. It is preferably used as the basis of alcoholic spirit drinks and other beverages. The invention therefore also provides a freeze distilled alcoholic beverage made with an alcohol produced according to the invention.

Preferably, the alcoholic beverage has a final ethanol concentration of at least 15%. Advantageously, the alcoholic beverage is freeze distilled vodka.

A third aspect of the invention provides an apparatus for distilling an alcohol, comprising a distillation column, a withdrawing system for removing a fraction from the distillation apparatus, at least one heat exchanger or cooler, a separation vat and a replacing system reintroducing for material from the separation vat to the distillation column, wherein, in use, an alcoholic aqueous fraction comprising ethanol and fusel oil is taken from the distillation apparatus via the withdrawing system, cooled in the heat exchanger or cooler to a point such that the fusel oil becomes substantially insoluble in the alcoholic aqueous fraction, the fusel oil is separated from the alcoholic aqueous solution in the separation vat and the alcoholic aqueous fraction is returned to the distillation column via the replacing system.

The invention is further described, for the purposes of illustration only, in the examples below, in which reference is made to the following figures. Modifications of the method within the scope of the present invention will be apparent to those skilled in the art.

Figure 1 is a diagram of the fusel oil removal apparatus in a freeze distillation process according to the invention. An alcoholic fraction is withdrawn from distillation column (1) by pump (2), at a temperature of 90°C (100 litres/h). This is passed sequentially through heat exchangers (3) and (4), in the latter of which it is cooled to -10°C by ammonia (8). The fraction then passes to separation tank (5) wherein the fusel oil is separated and removed (6). Pump (7) removes the residual alcoholic fraction, which passes through heat exchanger (3) wherein it is warmed to approximately 78°C before being returned to the distillation column.

Figure 2 is a diagram of a six-column distillation apparatus used for the production of agricultural alcohol. Mash (10) is fed into analyser (B). Slops (11) are discarded, whilst the distillate (12) passes to the rectifier (L). A fraction is taken at (13) for fusel oil removal, with the distillate passing to hydroselection column (F). Heads (14) are removed. Water (15) is added, heads passing in part to the feints and heads column (E), and the remaining fluid passes to the concentration column (K). The distillate is passed to the finishing column (S), from which agricultural ethanol is obtained (16).

Example 1.

Laboratory scale distillation procedure

Wheat grain is ground into flour and mixed with water, heated to 150°C for 3 minutes and allowed to cool to room temperature. Starch converting enzymes and yeast are added according to standard distillation protocols, and the mixture allowed to ferment for 3 days.

The fermented mash is then distilled on a distillation column according to standard procedures for the production of agricultural alcohol, as defined in EC Regulation No 1576/89. From this distillation column an alcoholic aqueous fraction is taken at a temperature of 90°C. This fraction is an aqueous alcoholic fraction with an alcohol content of 19.6% v/v.

The fraction is cooled to -8°C. Fusel oil separates from the alcoholic aqueous phase and rises to the top surface, where it has a yellowish oily appearance. The alcoholic aqueous phase remains liquid, and no ice crystals are formed.

Analysis of both phases gives the following results:

Substance	Oil phase (mg/l)	Aqueous phase (mg/l)
1-propanol	200	100
2-methyl-1-propanol	26000	3000
1-butanol	300	60
3-methyl-1-butanol	273000	8500
2-methyl-1-butanol	202000	6400
water	12.2 g/100ml	

A comparative assay, using the dilution methods of the prior art, yielded the following results:

Substance	Oil phase (mg/l)	Aqueous phase (mg/l)
1-propanol	300	200
2-methyl-1-propanol	31200	6500
1-butanol	600	120
3-methyl-1-butanol	341000	17000
2-methyl-1-butanol	253000	13000
water	10.5 g/100ml	

The results demonstrate superior removal of fusel oil from the aqueous phase by cooling than by dilution.

Example 2.

Industrial scale distillation

A distillation system comprising 6 distillation columns (obtained from Vogelbusch, Vienna, Austria) as shown in figure 2 is set up according to conventional parameters for the production of agricultural alcohol. In a continuous process, mash derived from whole wheat grain is fermented conventionally and introduced into the distillation apparatus at a rate of 8 m^3 per hour and heated to 90°C.

An aqueous fraction containing 25% ethanol is taken from the distillation column.

This fraction, having a temperature of approx. 85°C is led to heat exchanger 1 and is cooled as much as possible by means of the heat exchange with the lower phase from the separation vat. The liquid is subsequently led to heat exchanger 2 in which it is cooled to -10°C by direct evaporation of liquid ammonia.

Having been cooled down to this temperature, the liquid is led to a separation vat. Here the fusel oil rises to the surface from where it is drawn off.

The lower phase is pumped directly to heat exchanger 1 in which the liquid is heated to approx. 72°C and then led back to the column.

The distillation is continued through 5 columns, as shown in figure 2, with residuals being purified in the sixth column.

By applying this new method an improved separation of fusel oil is obtained, wherein an approximate improvement of 3% is achieved in respect of alcohols having more than 4 carbon atoms. The composition of the fusel oil removed varies according to the raw material used, but in general fusel oil removed by the method of the invention comprises slightly more ethanol, since the percentage of ethanol in the aqueous mixture will be slightly higher that that in a mixture which has been separated by a dilution method.

The distilled ethanol is mixed with water to produce vodka spirit. Freeze distilled vodka prepared using freeze distilled ethanol subjectively has a smoother flavour.

Claims.

1. A freeze distilled alcohol.

2. A freeze distilled alcoholic beverage comprising freeze distilled alcohol according to claim 1.

3. Freeze distilled vodka.

4. A process for removing fusel oil from an aqueous alcoholic medium, comprising the steps of:

(a) cooling the medium to effect separation of fusel oil from the medium; and

(b) removing at least part of the fusel oil from the medium.

5. A freeze distillation process for preparing a freeze distilled alcohol, the process comprising partial or complete removal of fusel oil by the steps of:

(a) removing an alcoholic aqueous fraction comprising ethanol and fusel oil from the distillation;

(b) cooling the fraction to reduce the solubility of the fusel oil therein; and

(c) separating the aqueous fraction from the fusel oil. and returning the thus separated aqueous fraction to the distillation.

6. A process according to claim 5, wherein the distillation process comprises a single distillation step.

7. A process according to any one of claims 4 to 6, wherein the alcoholic aqueous fraction comprises between 20% and 30% ethanol.

8. A process according to any one of claims 4 to 7, wherein the alcoholic aqueous fraction is taken from the distillation column at a temperature of between 80 and 95°C.

The Patent Office

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Claims searched: 1-15

Examiner: L.V.Thomas
Date of search: 4 March 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C6E (EBA, EC, EJF, EJH, EJX, EJY)

Int Cl (Ed.6): C12F; C12G; C12H

Other: Online: WPI, CLAIMS

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB 2261442 A	(Pollard) see p.1 ll.4-25 and p.2 l.27 - p.3 l.3	4,9,13
X	GB 1570944	(Douwe Egberts) see p.2 l.62 - p.3 l.17 and p.3 ll.35-54	4-6,9,13
X	US 5304384	(Murray et al.) see col.3 ll.44-68 and col.4 ll.14-19 and 44-52	4,9,13

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.